

## INTRODUCTION

Date:

---

**Instruction, Equipment and Safety**

---

**PLEASE READ THE FOLLOWING BEFORE YOUR FIRST DAY IN THE LAB.**

**Aim and Purpose of the Course**

Obviously the overall aim of the course is to give you experience in practical organic chemistry and help you generally to learn about organic chemistry as a part of medical/pharmacy course, but the purpose of the course will be clearer perhaps from the following five objectives:

**Objectives:** we hope that during the course you will

- 1) Experience the process of discovery for yourself and relate it to the role played by experiment in scientific investigations.
- 2) Become familiar with isolating and purifying compounds by solvent/solvent extraction.
- 3) Handle as wide a variety of compounds bearing different functional groups as possible.
- 4) Exploit the opportunities for learning about organic chemistry during the practical time to the full by asking your demonstrator questions.

**Continuous Assessment and the Practical Exam**

You will receive a mark for your laboratory work after each experiment. Credit for an experiment will be based on attendance, and completion of the experiment to your demonstrators' satisfaction. He will be looking at a number of different things such your neatness and tidiness while working in the laboratory. Your demonstrator will grade your book like this:

A = Excellent result

B = Satisfactory

C = poor work

This grading will count towards your final grade and will help you to assess how well you are progressing in your practice of organic chemistry. For this reason, your demonstrator will discuss the assessment with you when he grades the experiment at the end of the practical period.

## **Experimental Method and Write-up**

No note books are required. Spaces are provided at appropriate places in the manuals for you to record your observations, results etc. These must be written in during the laboratory period and graded by your demonstrator before you leave.

## **General Instructions**

This course deals with a number of test tube reactions which illustrate many of the functional groups covered in the lecture course. These test tube experiments are to be done during the first half period that you are in the lab.

The first experiments involve important practical techniques. These experiments are followed by experiments which follow the lecture course closely, so the lectures and practical are all part of the same organic chemistry course.

When you first come into the laboratory you will be allocated a certain cupboard containing most of the apparatus required for this terms work. Make sure all your apparatus is returned to this cupboard at the end of every practical.

Additional supplies of more special apparatus is also available for common use, but of limited supply. It is essential that this apparatus is returned clean at the end of each practical.

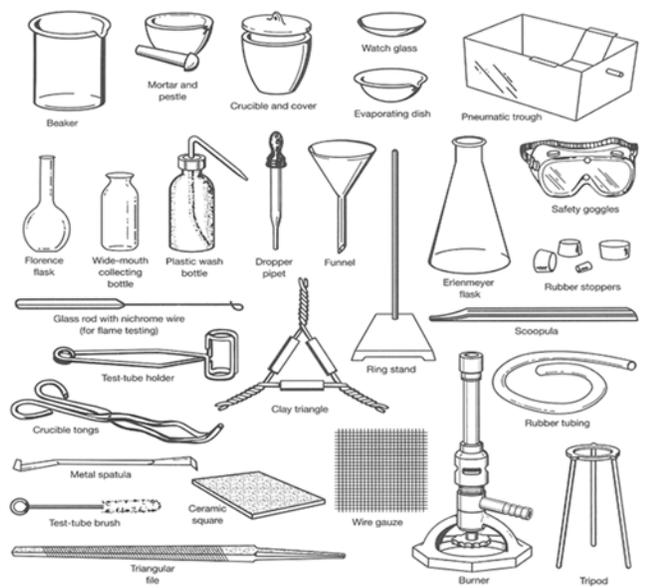
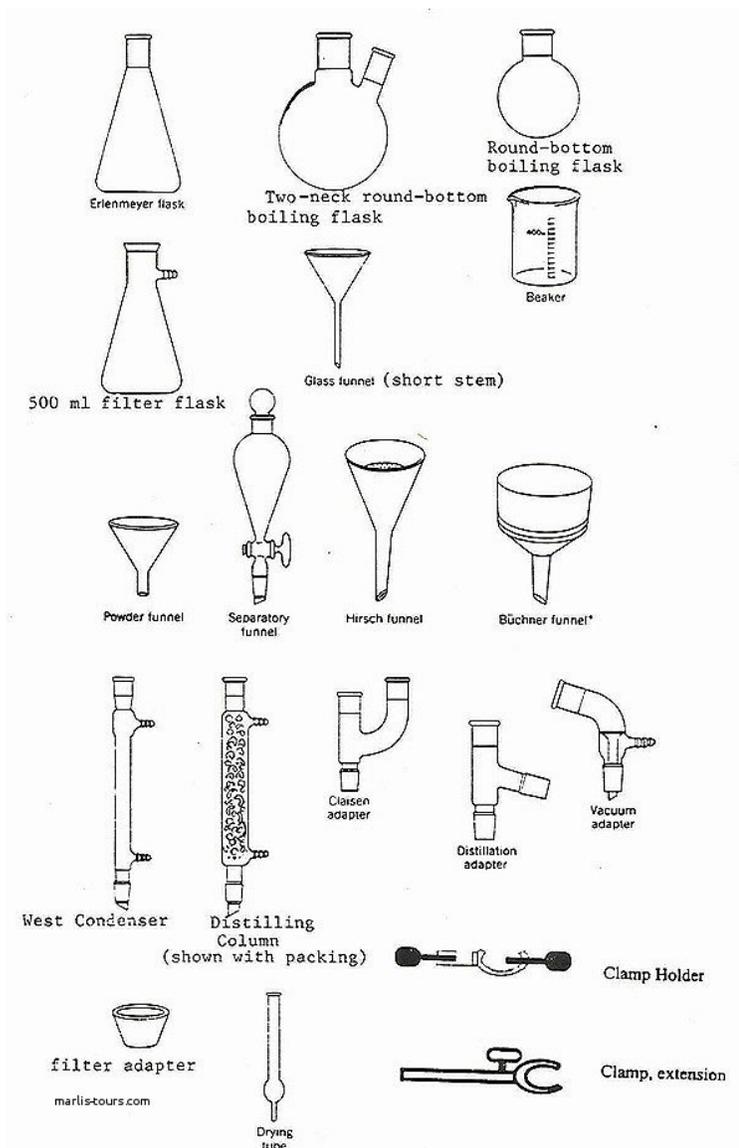
Please refer to the lecture material before you come to the laboratory so that you are familiar with the organic chemistry involved before you carry out any reaction.

## **Grading**

Thirty percent of your final grade will come from the practical part of the course. At the end of the course there will be a final practical exam. In addition, there will be six “drop quizzes”, five of which will count towards your grade. These “drop quizzes” will be short 5-minute test which will come without warning. They are designed to encourage you to read the instructions concerning the experiment before you come to the lab.

Attendance and Reports	10 degree
Drop quizzes Midterm	5 degree
Final Exam	15 degree

# Laboratory Equipment



## **List of Glassware and Equipment**

- 1) Condenser
- 2) Round-bottomed flask (50 mL and 100 mL)
- 3) Distilling head.
- 4) Adaptors.
- 5) Stoppers.
- 6) Separating funnels.
- 7) Beaker (50 mL, 100 mL, 250 mL and 400 mL).
- 8) Conical flask (100 mL and 250 mL).
- 9) Buchner funnel.
- 10) Buchner flask.
- 11) Funnel.
- 12) Glass rod.
- 13) Capillary tubes.
- 14) Test tubes.
- 15) Washing bottles.
- 16) Test tube rack.
- 17) Stand.
- 18) Clamps.
- 19) Test tube holder.
- 20) Heating Mantel 50 mL.
- 21) Watch glass.
- 22) Brush.

## Safety

A chemistry lab can be a dangerous place. If you work with care, however, you ought to survive and not eliminate your neighbors. Therefore: -

- 1) **ALWAYS** wear safety glasses in the lab. You may only be sitting at your bench writing in your manual, but your neighbor's distillation may explode.
- 2) **NEVER**, but never, allow ANY organic compound on your skin or breathe in the dust from a solid or spray from a liquid.

Some compounds are labelled as particularly dangerous. Carcinogenic ones cause cancer, some apparently harmless ones, like benzene, are very toxic indeed.

**ALL ARE LETHAL IN SUFFICIENT QUANTITY.**

Rubber gloves are available to protect your hands.

- 3) **NEVER** boil organic compounds in the open lab or allow gases to escape, use the fume cupboard.
- 4) **BEWARE of FIRE**. Know where the fire extinguishers are. Look around you before lighting your burner. In particular, make sure no one is using ether or petrol nearby.
- 5) **HANDLE** glass-ware **CAREFULLY**. Use quick fit apparatus, and watch for chipped or cracked apparatus: return it to the preparation room.
- 6) **REPORT** all accidents to your demonstrator. You may think you are "all right" but it is not worth taking chances.

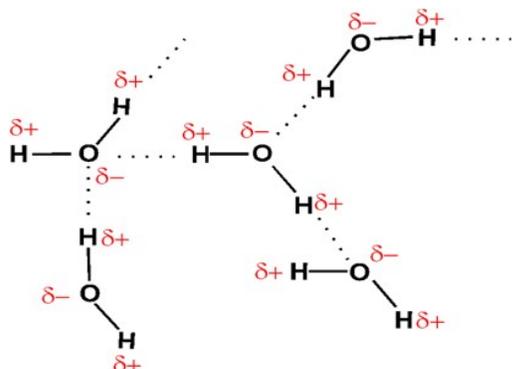
Keeping your bench clean is most important, always clean up at all times. You will have your grade reduced if you keep it in an untidy mess, the same applies to your locker.

**EXPERIMENT 1**

Date:

**Solubility**

General Rule: Like dissolve like



Water

polar
H-bond donor
H-bond acceptor
Solvates ions

**Test-tube 1**

- Place 1 mL of distilled water in the test tube.
- Add 0.5 mL of hexane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).
- Shake.

**Observation**How many layers are formed?  layer(s) is(are) formedi.e. hexane and water  $\left\{ \begin{array}{l} \text{do} \\ \text{do not} \end{array} \right\}$  mix

Hexane is

- non-polar
- non H-bonding
- does not solvate ions

**Test-tube 2**

- Place 1 mL of distilled water in the test tube.
- Add 0.5 mL of ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ).
- Shake.

**Observation**How many layers are formed?  layer(s) is(are) formedi.e. ethanol and water  $\left\{ \begin{array}{l} \text{do} \\ \text{do not} \end{array} \right\}$  mix

**Test-tube 3**

- Place 1 mL of distilled water in the test tube.
- Add 5 drops of 1-hexanol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ )
- Shake

**Observation**

How many layers are formed?  layer(s) is(are) formed

i.e. hexanol and water { do } mix  
  { do not }

In hexanol, the ratio of water insoluble “part” to water soluble “part” is high.

**Test-tube 4**

- Place 1 mL of distilled water in the test tube.
- Add 1 mL of ether ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ).
- Shake.

**Observation**

How many layers are formed?  layer(s) is(are) formed

i.e. ether and water { do } mix  
  { do not }

- Add one drop of red dye (in water) to the ether/water mixture.  
(The red dye is a dilute solution of potassium permanganate.)

**Observation**

The clear, ether layer is the ..... one.

- Add 1 mL of ethanol to the ether/water mixture.

**Observation**

-----  
-----

**Test-tube 5**

- Place 1 mL of distilled water in the test tube.
- Add 1 mL of chloroform ( $\text{CHCl}_3$ ).
- Shake.

**Observation**

How many layers are formed?  layer(s) is(are) formed

i.e. chloroform and water  $\left\{ \begin{array}{l} \text{do} \\ \text{do not} \end{array} \right\}$  mix

Ether and chloroform are good solvents for extraction from aqueous solutions

**Test-tube 6**

- Place 1 mL of chloroform in the test tube.
- Add 1 mL of azo-dye solution (in water).
- Shake.

**Observation**

- o Color of top layer .....
- o Color of bottom layer (CHCl<sub>3</sub>) .....

- Shake vigorously

**Observation**

- o Color of top layer .....
- o Color of bottom layer (CHCl<sub>3</sub>) .....

Therefore, the dye is preferentially soluble in .....

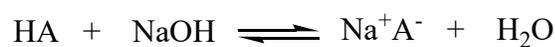
- Add 3 drops of 5% NaOH solution to the dye/CHCl<sub>3</sub>/H<sub>2</sub>O mixture and shake well

**Observation**

- o Color of top (alkali) layer .....
- o Color of bottom layer (CHCl<sub>3</sub>) .....

Therefore, the dye is preferentially soluble in .....

HA = Azo dye



HA (light yellow) soluble in  $\left\{ \begin{array}{l} \text{water} \\ \text{CHCl}_3 \end{array} \right.$

Na<sup>+</sup>A<sup>-</sup> (deep yellow) soluble in  $\left\{ \begin{array}{l} \text{water} \\ \text{CHCl}_3 \end{array} \right.$

## EXPERIMENT 2

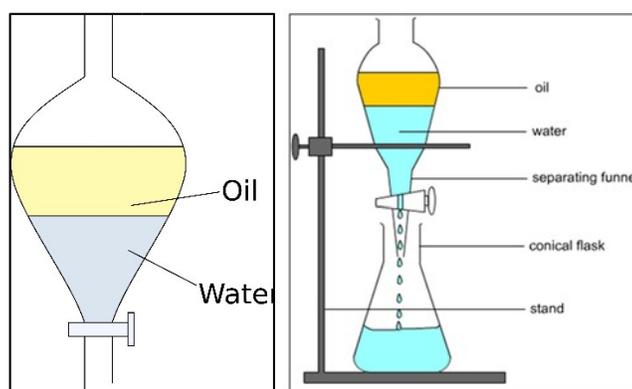
Date:

## Extraction

It is evident from the test-tube reactions that a compound dissolved in one solvent can be extracted into another solvent if:

- It is more soluble in the second solvent; and
- The two solvents are immiscible.

On a preparative scale these extractions are carried out in a “separating funnel”, which is constructed to allow easy separation of two immiscible solutions.



**Figure 1:** Diagram of separating funnel apparatus.

The objective of this experiment is to make you familiar with this technique.

**Table 1:** List of common solvents that can be used for extraction from water.

Solvent	Formula
Hexane (light petrol)	$C_6H_{14}$
Benzene	$C_6H_6$
Diethyl ether (ether)	$(C_2H_5)_2O$
Ethyl acetate	$CH_3COOC_2H_5$
Chloroform	$CHCl_3$
Carbon tetrachloride	$CCl_4$

**NOTE** that methanol, ethanol, and acetone are miscible with water and cannot be used for extraction from water.

## Separation of Mixture of Basic and Acidic Compounds

### Background principles



### Solubility

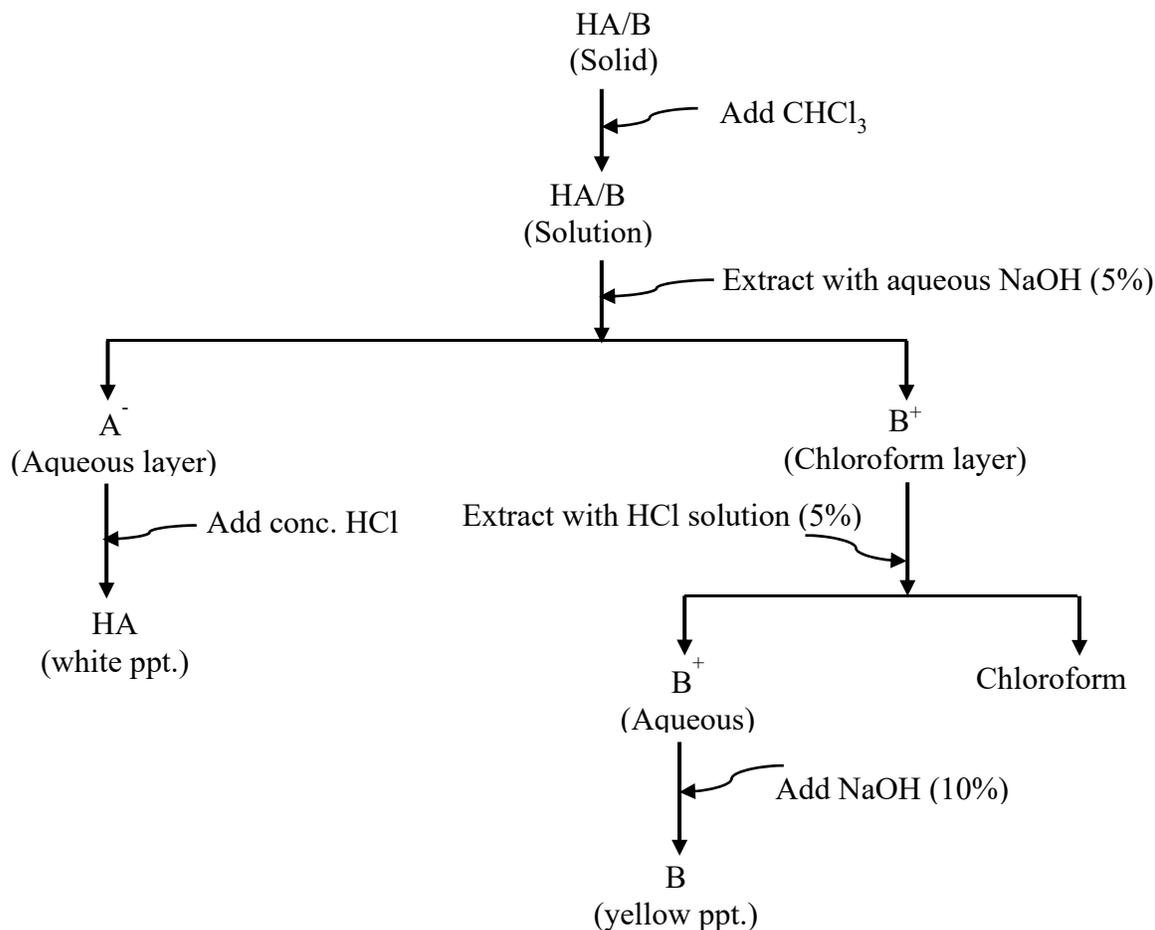
Insoluble in water

Soluble in water

Soluble in organic solvents

Insoluble in organic solvents

If we have a mixture of acidic (HA) and basic (B) organic compounds, which are soluble in organic solvents but insoluble in water, then may be separated by making use of the differential solubility in acid or alkaline conditions above. The scheme required to achieve this separation can be represented by:



## Procedure

- In a 50 mL conical flask weigh approximately 2 g of a mixture of benzoic acid ( $C_6H_5COOH$ ), HA and *m*-nitroaniline.
- Add 25 mL of chloroform.
- Transfer the solution to a 50 mL separating funnel, using a funnel (Figure 1).

## Solvent Extraction General Procedure

- Clamp the separatory funnel securely with the tap lubricated with Vaseline and closed.
- Pour in the chloroform solution through a funnel and use in a little extra chloroform to wash in the last traces of a powder sticking to the walls of the flask and to the funnel.
- Add 20 mL of 10% sodium hydroxide solution to the separatory funnel through the funnel.
- Insert the stopper (lubricated with Vaseline) and shake the separating funnel to mix the layers thoroughly, releasing the pressure via the top at frequently intervals.
- Allow the layers to separate.
- Remove the stopper. Run off the lower layer into a 50 mL conical flask; not too fast or you will create a vortex. Close the tap when the bore of the tap contains the last of the lower layer.

The chloroform layer contains?

.....

The aqueous layer contains?

.....

- Run the upper (aqueous) layer into a 100 mL conical flask.
- Add to upper layer conc. HCl until no whiter precipitate forms. It may be necessary to cool the solution.

The precipitate is

.....

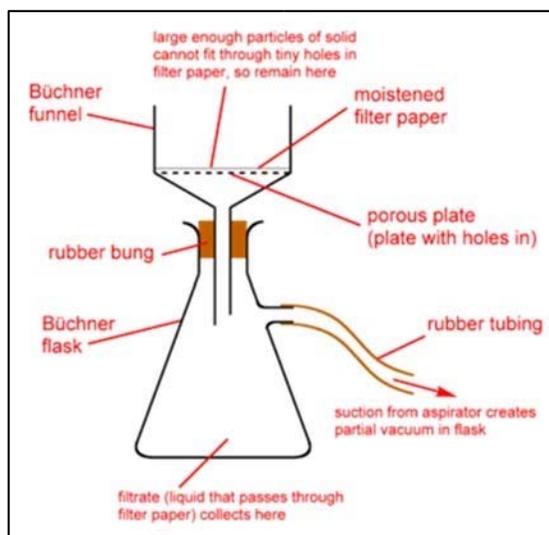
Allow the solution to cool and then suction filter off the solid, wash it with a little cold water and dry in an oven.

## Suction Filtration

Apparatus: Buchner funnel, flasks and filter paper (Figure 2).

- 1) Choose the correct size of filter paper, wet it all over with water and place it centrally in the funnel.
- 2) Briefly apply suction to secure the paper firmly in place.
- 3) Pour in the slurry of crystals. Do not fill to more than 2/3.
- 4) Use filtrate (mother-liquor) to wash in any crystals which remains stuck to the walls of the flask.
- 5) To wash the crystals with cold water, first release the vacuum slurry the crystals taking care not to damage the filter paper then reapply the suction.

**To dry**, place the crystals on a clean filter paper, and cover with another piece of filter paper.



**Figure 2:** Buchner funnel.

Then put chloroform layer back into separating funnel.

Extract with 20 mL of 10% HCl solution.

The chloroform layer contains? .....

The aqueous layer contains? .....

Separate the layers.

Keep the upper aqueous layer and put the lower chloroform layer into the residue bottle.

To the aqueous layer, add 10% NaOH until no further precipitation takes place.

The precipitate is .....

Suction filter the solid, wash with a little water and dry in the air at room temperature.

### **Caution**

- Since most organic chemicals are hazardous in some way (e.g. inflammable, poisonous vapor or poisoning through skin) take care not to get any on your hand.
- The *m*-nitroaniline is highly colored and toxic so you will be able to observe any contamination.
- If you get any, on your skin wash your skin with soap and water. Do not wash with an organic solvent, this would assist passage of the contaminant through your skin.

### **Questions**

Predict the outcome of the following extractions?

- 1) Benzoic acid dissolved in ether.
  - a) Extract with aqueous HCl .....
  - b) Extract with H<sub>2</sub>O .....
  - c) Extract with aqueous NaOH .....
- 2) Aniline dissolved in ether.
  - a) Extract with aqueous HCl .....
  - b) Extract with H<sub>2</sub>O .....
  - c) Extract with aqueous NaOH .....

Please submit your sample to your demonstrator before you leave

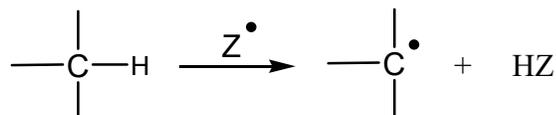
**EXPERIMENT 3**

Date:

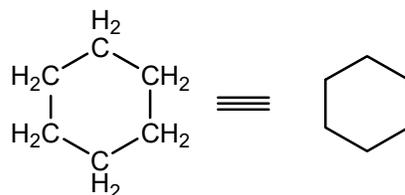
**Aliphatic Hydrocarbon (Bonding)**  
**(Alkanes and Alkenes)**

In general C – H and C – C bonds in alkanes are unreactive towards polar reagents.

Reaction generally occurs by the formation of radicals in the presence of a suitable initiator (Z.).



Consider the reaction of cyclohexane and bromine

**Test-tube 1**

- Take 1 mL of cyclohexane.
- Add 3 drops of Br<sub>2</sub>/CCl<sub>4</sub> solution.  
Does the bromine color remain? .....
- In the presence of light from the sun or a UV lamp, the bromine undergoes homolytic fission and readily reacts with the cyclohexane. What occurs to the contents of the tube in sunlight?

.....  
 .....

Write the chemical equation

.....  
 .....

- Dip a clean glass rod into conc. NH<sub>4</sub>OH and hold the glass rod over the mouth of the test tube. What colors?

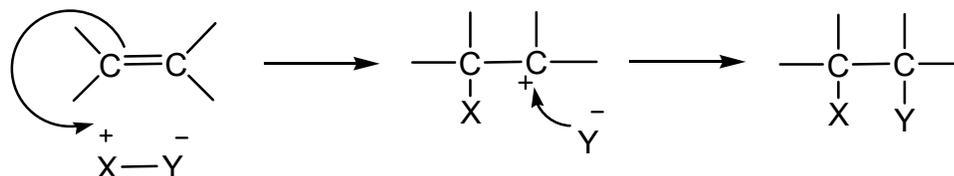
.....  
 .....

What you are observing is the formation of  $\text{NH}_4^+\text{Br}^-$ ?

This is a test for the presence of HBr.

## Test-tube 2      Addition of Bromine to an Alkene

Alkenes undergo polar addition reactions initiated by electron rich system of the double bond.



- Take 3 drops of cyclohexene.
- Add 3 drops of  $\text{Br}_2/\text{CCl}_4$  solution.

### Observation

Did bromine color disappear?

.....  
 .....

- Add 1 mL  $\text{Br}_2/\text{CCl}_4$  solution.
- Shake.

### Observation

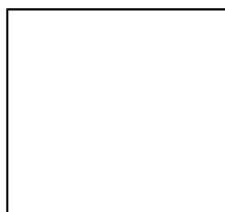
.....  
 .....

- Test for the presence of HBr.

### Observation

.....  
 .....

Pour the contents of the tube into the residue bottle. If you carried out an evaporation of the  $\text{CCl}_4$  and excess bromine, what would remain?



Write the chemical equation

.....  
.....

### Test-tube 3

Reaction with dil.  $\text{KMnO}_4$  solution is also a test for the presence of carbon-carbon double bonds.

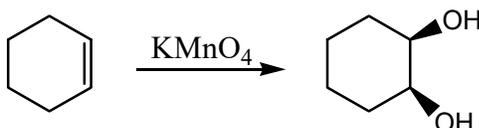
The double bond of an alkene is easily oxidized to a di-OL.

- Take 3 mL of dil.  $\text{KMnO}_4$  solution.
- Add 3 drops of cyclohexene.
- Shake.

### Observation

.....  
.....  
.....

The cyclohexene undergoes oxidation (the permanganate is reduced) and the di-OL is formed.



### Questions

- 1) Write the chemical equation for the addition of bromine to 2-pentene?

.....  
.....  
.....  
.....

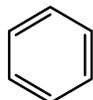
- 2) Write the equation for the oxidation of propene?

.....  
.....  
.....

## EXPERIMENT 4

Date:

## Aromatic Hydrocarbons

**Test-tube 1**      **The Reactions of Bromine with Benzene**

Benzene

- Take 1 mL of 90% acetic acid (solvent).
- Add 5 drops of benzene.
- Add 5 drops of Br<sub>2</sub>/CCl<sub>4</sub>.

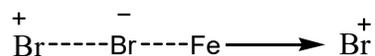
**Observation**

Does the bromine color disappear?

.....

.....

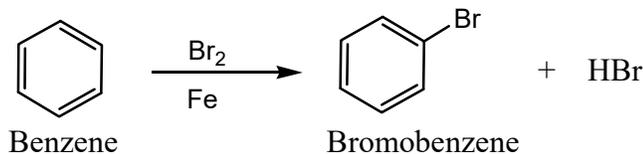
Pour the contents of the tube into the vial containing the iron powder, shake. Polarization of the bromine occurs



The positive bromine species is a better electrophile than molecular bromine.

Does the bromine color disappear? .....

.....



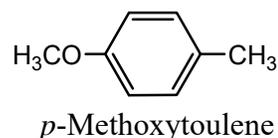
This is electrophilic aromatic substitution.

**Test-tube 2**      **Benzene with Potassium Permanganate**

- Take 1 mL of dilute aqueous KMnO<sub>4</sub> solution.
- Add 2 drops of benzene.
- Shake.

Does the permanganate color disappear?

.....

**Test-tube 3**      ***p*-Methoxytoluene with KMnO<sub>4</sub>**

Alkyl side chains undergo oxidation while the aromatic ring is unaffected.

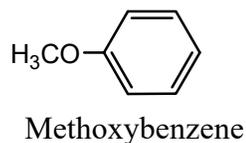
- Take 1 mL of dilute aqueous KMnO<sub>4</sub> solution.
- Add one drop of *p*-methoxytoluene.
- Shake.

**Observation**

.....  
.....

Write the chemical equation of the reaction

.....  
.....  
.....

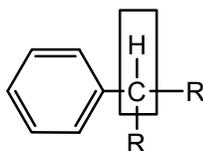
**Test-tube 4**      **Anisole (Methoxybenzene) with KMnO<sub>4</sub>**

- Take 1 mL of dilute aqueous KMnO<sub>4</sub> solution.
- Add 2 drops of anisole (methoxybenzene).
- Shake.

Does the permanganate color disappear?

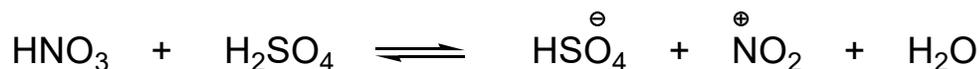
.....  
.....  
.....

Therefore, oxidation requires

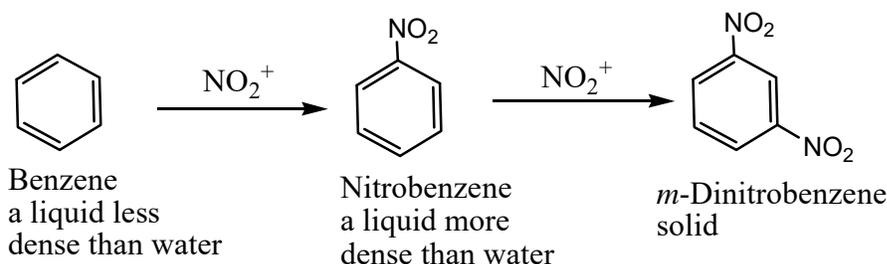


**Test-tube 5 Nitration of Benzene**

- Take 1 mL of nitrating mixture (conc. H<sub>2</sub>SO<sub>4</sub> + conc. HNO<sub>3</sub>).
- Add 5 drops of benzene.
- Shake well.
- Reactive electrophile is NO<sub>2</sub><sup>+</sup>, produced as follows:



- Take about 20 mL of distilled water in a small beaker.
- Pour reaction mixture into this water.

**Observation**

The main product of my reaction is .....

The first nitro group deactivates the ring to further attack and directs the second nitro group exclusively to the meta position.

**Questions**

How can you test for the formed hydrogen bromide from the reaction of benzene with bromine? Explain by equation

.....  
 .....  
 .....

Can HBr be produced from the reaction of bromine with alkene?

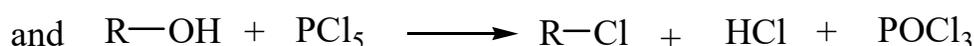
.....  
 .....  
 .....

**EXPERIMENT 5**

Date:

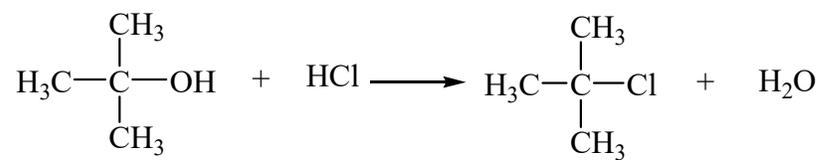
**Hydroxy Compounds (Alcohols and Phenols)****Reaction A****Test-tube 1      Preparation of Alkyl Halide from Alcohol**

In practice



These are the reactions generally carried out.

Tertiary alcohols, however, do react readily with hydrogen halides.

**Procedure**

- Take 1 mL of conc. HCl.
- Add 10 drops of *t*-butanol.
- Shake.
- Place the tube in hot water bath.

**Observation**

.....

.....

**Reaction B      Oxidation of Alcohols**

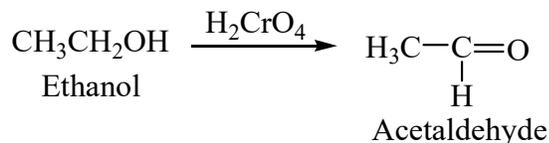
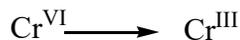
Reaction with an oxidizing agent e.g.  $\text{KMnO}_4$ ,  $\text{H}_2\text{CrO}_4$ , is an important synthesis of aldehydes, ketones and carboxylic acids.

**Test-tube 2**

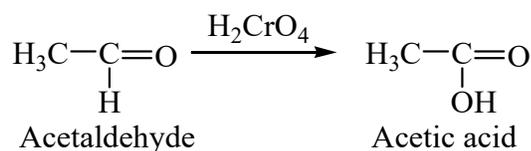
- Take 1 mL of chromic acid.
- Add 5 drops of ethanol (primary alcohol).
- Place the tube in hot water bath.

**Observation**

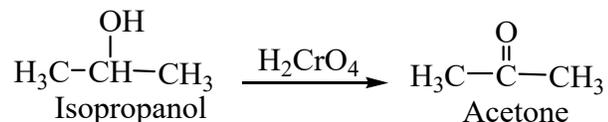
The color of the solution changed rapidly from ..... to .....



**NOTE:** The sweet smell of the aldehyde. Further oxidation occurs under these conditions.



Secondary alcohols are oxidized to ketones under these conditions.



Ketones and tertiary alcohols are resistant to further reaction.

**Test-tube 3**

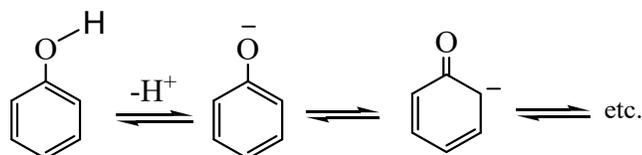
- Take 1 mL of chromic acid.
- Add 5 drops of *t*-butanol (tertiary alcohol).
- Place the tube in hot water bath.

**Observation**

.....  
 .....

**Reaction C      Acidity of Phenols**

Resonance stabilization of the charge in the anion is responsible for phenols being weak acids.



Phenols are stronger acids than alcohols.

**Test-tube 4**

- Take 1 mL of aqueous phenol solution.
- Add 1 drop of bromothymol blue.  
(pH color change of bromothymol blue; (yellow at pH 6.2) to (blue at pH 7.6).

**Observation**

The color of the solution .....

**Conclusion**

The solution has a pH of .....

**Test-tube 5**

- Take 1 mL of aqueous phenol solution.
- Add 1 drop of bromophenol blue.  
(pH color change of bromophenol blue; (yellow; pH 3.0 to blue; pH 4.6).

**Observation**

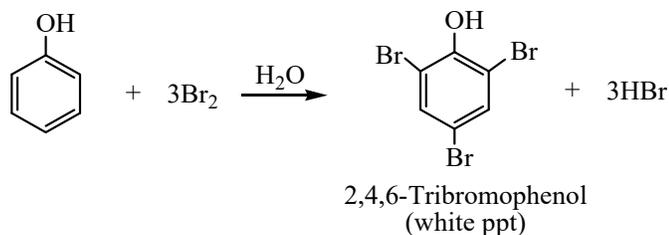
The color of the solution .....

**Conclusion**

The solution has a pH of .....

The phenol solution therefore has a pH somewhere between ..... and .....

Phenol is not sufficiently acidic to liberate CO<sub>2</sub> from Na<sub>2</sub>CO<sub>3</sub>.

**Reaction D****Electrophilic Substitution in Phenol****Test-tube 6**

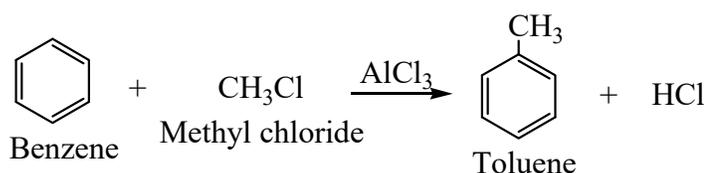
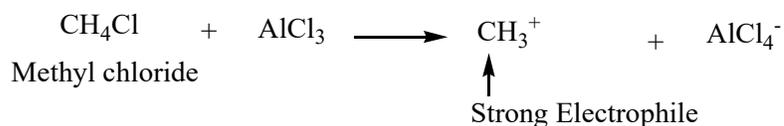
- Take 3 drops of the aqueous phenol solution.
- Add 2 mL of bromine water.

**Observation**

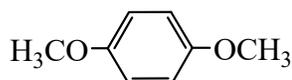
.....

**Reaction E**      **Reaction with FeCl<sub>3</sub>****Test-tube 7**

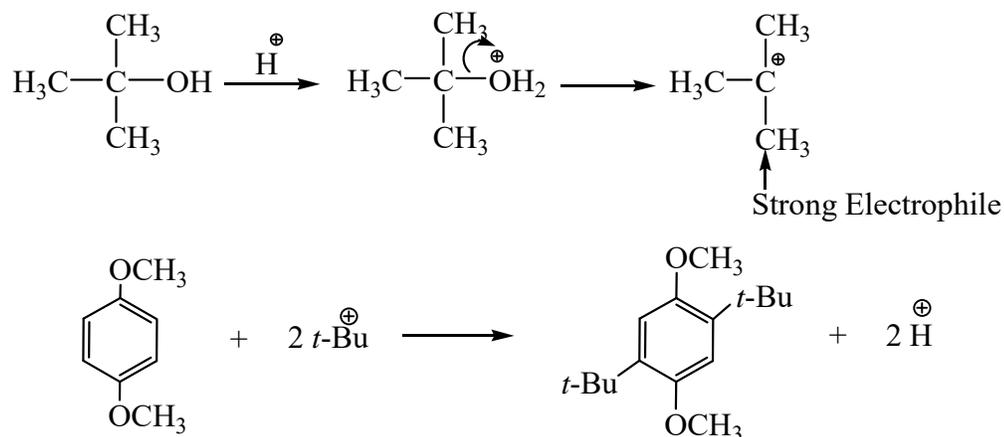
- Take 3 drops of the aqueous phenol solution.
- Add 2 drops of FeCl<sub>3</sub> solution.

**Observation****Reaction F**      **Alkylation of an Aromatic Ring****Friedel Craft's Reaction****Test-tube 8**

- Take 1 mL of 1,4-dimethoxybenzene in acetic acid.



- Add 5 drops of *t*-butanol.
- Add 2 drops of conc. H<sub>2</sub>SO<sub>4</sub>.
- Place the tube in the hot water bath.



- Pour on to ice in a small beaker.

**Observation**

.....

.....

.....

**Question**

1) Write the chemical equation for phenol with ferric color

.....

.....

2) Write the chemical equation for preparation of toluene from benzene.

.....

.....

## EXPERIMENT 6

Date:

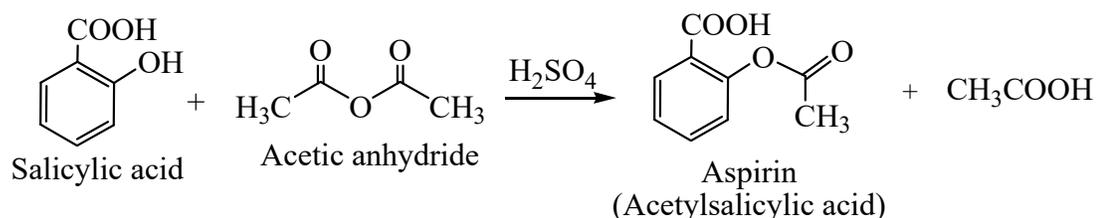
**Preparation of Aspirin**

Salicylic acid and many of its derivatives are antipyretics and analgesics but the acetyl derivative is not having any bad side-effects. Willow bark tea, which contains salicylic acid, was known to Hippocrates as a valuable analgesic ("Salicylic acid" is derived from the latin salix, willow).

Acetylsalicylic acid was first prepared in 1854 by a German called Gerhardt, but it was not until forty years later that its medicinal value was recognized when Hoffmann, a German chemist, tried it on his father and found that it eased the old man's rheumatic pains.

Aspirin is therefore one of the earliest examples of the alternation in chemotherapeutic properties that can result from a seemingly minor alteration in molecular structure. Of course, aspirin itself can cause undesirable side effects in some people (gastric irritation and skin rashes) but these effects are not nearly (headache, dizziness, mental confusion, nausea, etc.).

According to one textbook "over 27 million pounds of aspirin are consumed yearly in the United States (sufficient to treat over 17 billion headaches)". Thus though aspirin is widely used its mechanisms of action are still unknown. Both the antipyretic and the analgesic effects for many years thought to be central; that is, its drug somehow affects the temperature control center (the hypothalamus) and the pain center (subcortical regions, probably the thalamus) of the brain. More recently a new hypothesis of action has been advanced. The drug may act locally to reduce fever, pain and inflammation by inhibiting cellular release of a chemical which mediates these defense reaction, in particular the secondary defense mechanism (its substances including histamine, kinins and prostoglandines).

**Procedure**

- Weigh out 5 g of salicylic acid.
- Place the salicylic acid in a 125 mL conical flask.
- Add 10 mL of acetic anhydride in the hood.

- Add 1-2 mL of conc.  $\text{H}_2\text{SO}_4$ .
- Stopper flask with plug of cotton wool.
- Swirl the reaction mixture for 10 minutes.
- After 10 minutes, add 25 mL of ice water and swirl for 10 minutes.
- Collect the precipitate in a small Buchner funnel.
- Wash it with 10 mL of ice water.
- Dry the product in the air.
- Weigh and determine the melting point.

### **Ferric Chloride Test for Phenol**

Ferric chloride forms complexes with enols and phenol. These complexes are usually dark in color, dark purple and dark green being common. These colored complexes form the basis of a test for phenols.

### **Procedure**

- Place 2 mL of ferric chloride solution in the test-tube (Ferric chloride solution has a pale yellow color).
- Add to it a few crystals of salicylic acid.

Repeat the test but instead of using salicylic acid, add a few crystals of your product.

### **Observation**

.....  
.....  
.....

Weight of Aspirin obtained = ..... g.

Melting point of Aspirin = ..... °C.

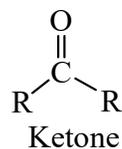
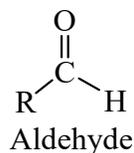
### **Questions**

What is the structure of Aspirin?

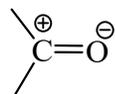
## EXPERIMENT 7

Date:

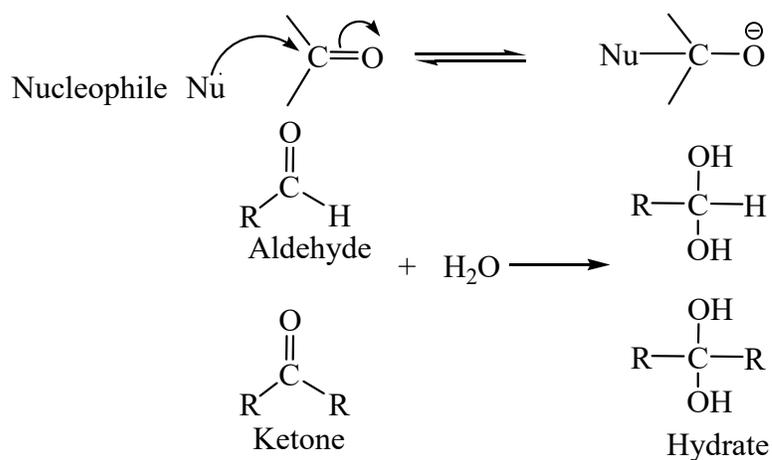
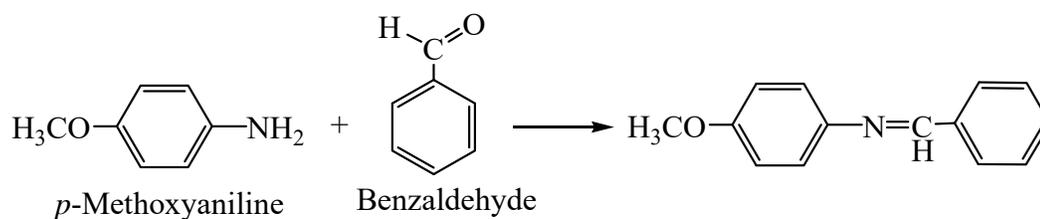
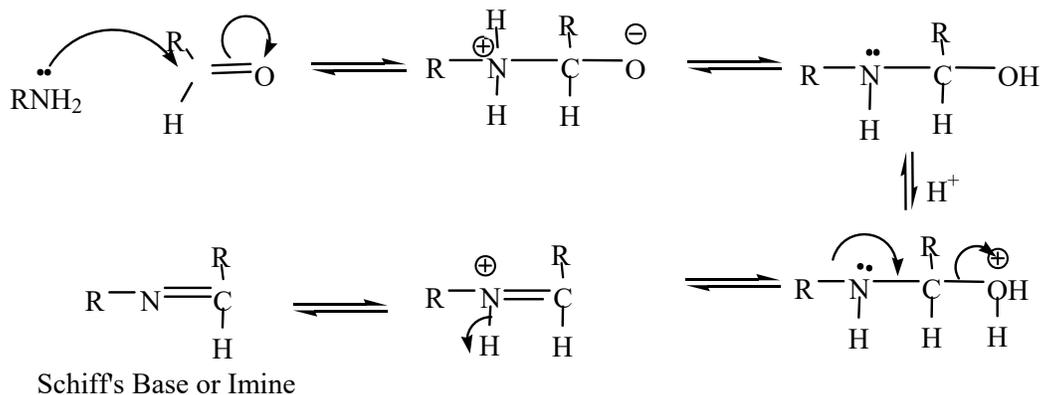
## Aldehydes and Ketones



Aldehydes and ketones are characterized by carbonyl group-polarized double bond.



Attack by nucleophiles therefore occurs at the C<sup>+</sup> end.

**Reaction A      Carbonyl Compounds with Amines**

**Test-tube 1**

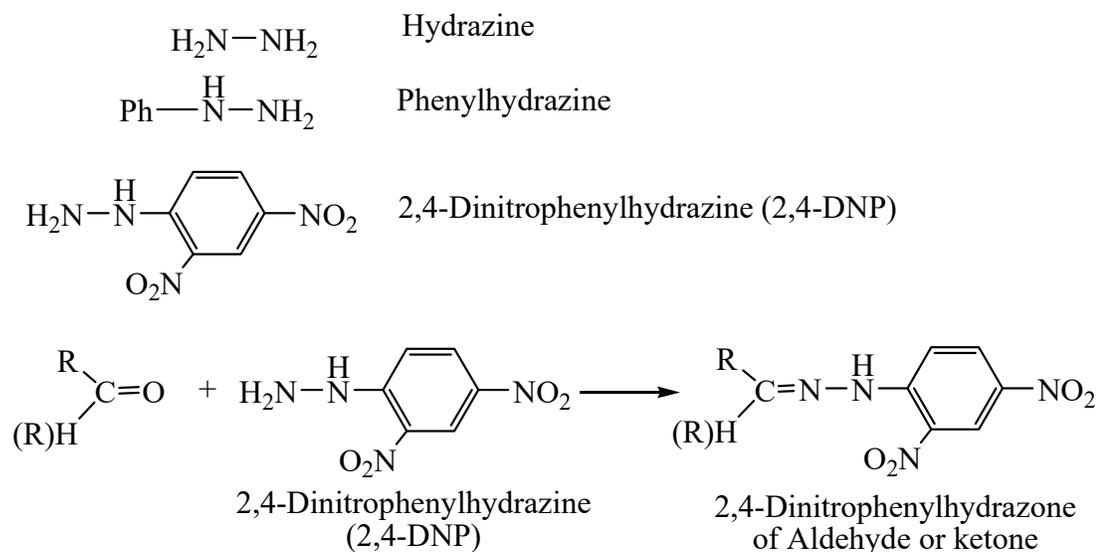
- Take 0.5 mL of ethanol.
- Add 5 drops of benzaldehyde.
- Add 1 mL of *p*-methoxyaniline (*p*-Anisidine) in ethanol-water.
- Shake.
- Place in a hot water bath.
- Cool the tube and add 1 drop of water.

**Observation**

.....

.....

.....

**Reaction B      2,4-Dinitrophenylhydrazone Formation**

The reaction is used to identify aldehydes and ketones, as the m.p. of a 2,4-DNP is characteristic.

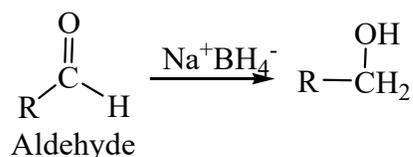
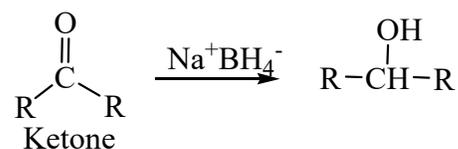
**Test-tube 2**

- Take 1 mL of 2,4-dinitrophenylhydrazone reagent.
- Add 1 drop of benzaldehyde or acetaldehyde or acetone.

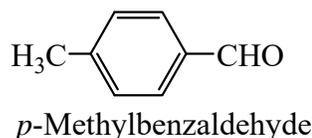
**Observation**

.....

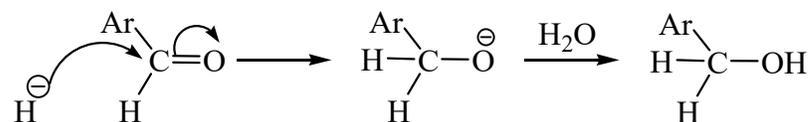
.....

**Reaction C**      **Reduction**NaBH<sub>4</sub> = Sodium borohydride**Test-tube 3**

- Take 1 mL of ethanol.
- Add 5 drops of *p*-methylbenzaldehyde.



- Add 2 mL of NaBH<sub>4</sub> solution.
- Allow to stand.



- Add a few pieces of ice to a small beaker.
- Pour into the reaction mixture.

**Observation**

.....

.....

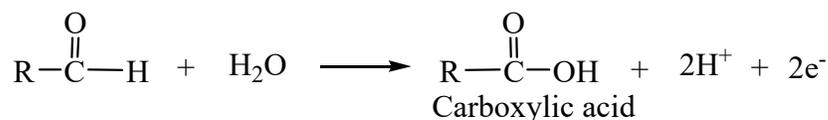
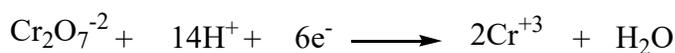
.....

**Reaction D**      **Oxidation**

Both aldehydes and ketones react with the former being much more reactive.

**Test-tube 4**

- Take 1 mL of 90% acetic acid (the solvent).
- Add 5 drops of benzaldehyde.
- Add 10 drops of chromic acid (take care).
- Place the tube in the hot water bath.



- Place about 10 mL of cold water in a small beaker.
- Add the contents of the tube.

### Observation

.....

.....

.....

### Reaction E      Distinguishing Test

Tollen's reagent (a weak oxidizing agent) – ammonical silver nitrate with  $\text{NH}_4^+$  as the oxidant.

### Test-tube 5

- Take 2 mL of  $\text{AgNO}_3$  solution.
- Add 8 drops of 5%  $\text{NaOH}$  solution.
- Add ammonium hydroxide dropwise and with mixing until the black precipitate just dissolves. (This is Tollen's reagent)
- Divide the solution into 2-test-tubes.

### Reaction E (i)

- Add 1 drop of benzaldehyde to the sample of Tollen's reagent in the test-tube.
- Place the tube in the hot water bath.

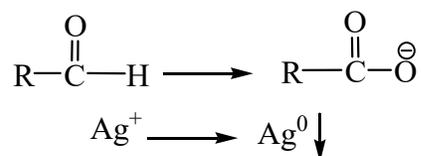
### Observation

.....

.....

.....

.....



**Reaction E (ii)**

- Add 1 drop of acetone to the sample of Tollen's reagent in the test-tube.
- Place the tube in the hot water bath.

**Observation**

.....  
.....  
.....

**Questions**

1) Write the equation represents the reduction of benzenaldehyde

.....  
.....  
.....  
.....  
.....  
.....

2) Write the equation represents the oxidation of *p*-methoxybenzaldehyde

.....  
.....  
.....  
.....  
.....  
.....

## EXPERIMENT 8

Date:

## Carbohydrates

Carbohydrates are compounds containing C, H, O and the H and O are present in the same proportion as in water. The word carbohydrate can be expressed as hydrates of carbon because molecular formulas of these compounds.

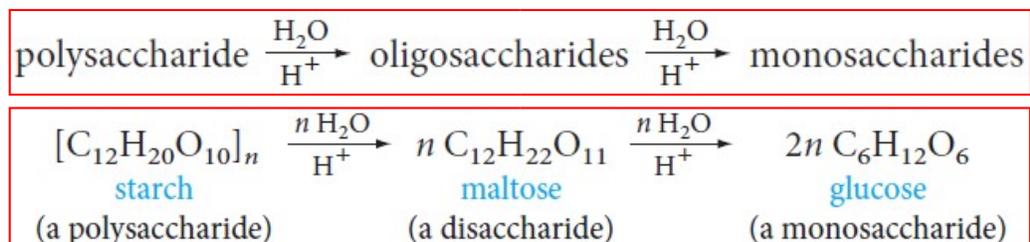
Example; Glucose has the molecular formula  $C_6H_{12}O_6$ , which might be written as  $C_6(H_2O)_6$ .

The chemistry of carbohydrates is mainly the combined chemistry of two functional groups: the hydroxyl group and the carbonyl group.

Carbohydrates are usually classified according to their structure as;

- 1) Monosaccharides: (glucose, galactose and fructose).
- 2) Disaccharides: (sucrose, maltose and lactose).
- 3) Polysaccharides: (starch and inulin).

The three classes of carbohydrates are related to each other through hydrolysis.



**Monosaccharides** (or simple sugars, as they are sometimes called) are carbohydrates that cannot be hydrolyzed to simpler compounds.

**Polysaccharides** contain many monosaccharide units—sometimes hundreds or even thousands. Usually, but not always, the units are identical. Example; starch and cellulose, contain linked units of the same monosaccharide, glucose.

**Oligosaccharides** (from the Greek oligos, few) contain at least two and generally no more than a few linked monosaccharide units. They may be called disaccharides, trisaccharides, and so on, depending on the number of units, which may be the same or different. Example; Maltose is a disaccharide made of two glucose units. Sucrose is made of two different monosaccharide units: glucose and fructose.

## Physical properties

Colorless solids, which decomposes on heating and therefore have no definite melting points. All are soluble in cold water except starch.

## General Reactions:

### Reaction A            Effect of Heat

#### Test-tube 1

Heat a small amount of the solid carbohydrate.

#### Observation

All give the smell of burnt sugar when burnt.

### Reaction B            Molisch's Test

#### Test-tube 2

- Take concentrated solution of the carbohydrate in water.
- Add equal amount of  $\alpha$ -naphthol solution.
- Carefully add excess amount of concentrated  $\text{H}_2\text{SO}_4$  inside the wall of the tube to form a heavy layer at the bottom.

#### Observation

All respond to Molisch's test.

A deep violet ring is produced at the interface.

- Shake the solution.

#### Observation

The violet color spreads through the whole solution.

### Reaction C            Conc. $\text{H}_2\text{SO}_4$ Test

#### Test-tube 3

- Take a small amount of the solid carbohydrate in dry tube.
- Add 1 mL of concentrated  $\text{H}_2\text{SO}_4$ .
- Heat carefully.

#### Observation

Observe the immediate blackening of the solid.

**Reaction D**      **Barfoed's Test: (Copper Acetate in Acetic Acid Solution)****Test-tube 4**

- Take 1 mL of sugar solution.
- Add 1 mL of Barfoed's reagent.
- Boil the soln. for one minute.

**Observation**

- Glucose and Fructose give red ppt. of cuprous oxide appears.
- Maltose (Malt sugar) gives red ppt. only after prolonged heating (more than 15 min) as it is hydrolyzed to glucose.
- Lactose (Milk sugar) gives red ppt. only after prolonged heating (more than 15 min) as it is hydrolyzed to glucose and galactose.
- Starch and Sucrose (Can sugar) give –ve result.

**Reaction E**      **Ammoniacal Silver Nitrate****Test-tube 5**

- Take 1 mL of sugar solution.
- Add 1 mL of dil. ammoniacal silver nitrate.
- Boil the soln. for one minute.
- Place the test tube on a water bath.

**Observation**

- Glucose, Fructose, Maltose (Malt sugar) and Lactose (Milk sugar); a silver mirror is produced in 1-2 minutes.
- Starch and Sucrose (Can sugar) give –ve result.

**Reaction F**      **Reduction of Fehling's Solution (A+B)****Test-tube 5**

- Take 1 mL of sugar solution.
- Add 1 mL of Fehling's solution (A+B).
- Boil the soln. for one minute.

**Observation**

- Glucose, Fructose, Maltose (Malt sugar), and Lactose (Milk sugar); Reduction takes place and a red ppt. of cuprous oxide is formed.
- Starch and Sucrose (Can sugar); –ve result.

## Reaction G Osazone formation

### Test-tube 6

- Take solid sugar, phenylhydrazine hydrochloride, and sodium acetate in the ratio of 1:2:3.
- Add 5 drops of water.
- Place in a hot water bath for 10-15 minutes.

### Observation

- Glucose and Fructose; yellow ppt. of the osazone appears after 10-15 minutes. Examine under the microscope, yellow needles aggregated in the form of sheaves.
- Maltose (Malt sugar); Forms yellow ppt. of osazone soluble in hot water, the yellow crystals of the osazone will appear only after cooling the soln. Examine the crystals under the microscope.
- Lactose (Milk sugar); Forms yellow ppt. of osazone soluble in hot water, the yellow crystals of the osazone will appear only after cooling the soln. Examine the crystals under the microscope.
- Starch and Sucrose (Can sugar); –ve result.



Glucosazone

or Fructosazone



Maltosazone



Lactosazone

## Reaction H Rapid Furfural Test

### Test-tube 7

- Take 1 mL of dil. sugar solution.
- Add 1 mL of  $\alpha$ -naphthol solution.
- Add 3 mL of conc. HCl.
- Boil in a water bath.

### Observation

- Glucose, Maltose (Malt sugar), and Lactose (Milk sugar); a violet color appears after some time.
- Fructose and Sucrose (Can sugar); an immediate violet coloration on boiling.

- Starch; Faint violet color after long time.

**Reaction I**            **Ketose test**

**Test-tube 8**

- Take 1 mL of dil. sugar solution.
- Add 2 mL of conc. HCl.
- Boil carefully.

**Observation**

- Fructose; observe the orange color is formed.
- Sucrose (Can sugar); Orange color.

**Reaction J**            **Hydrolysis by Acids**

**Test-tube 9**

- Take a suspension of starch in water.
- Add 3 mL of conc. HCl.
- Mix well
- Place on a boiling water-bath for 20 minutes.
- Cool.
- Add 2 drops of iodine soln. to ½ ml. of the soln. in another tube.

**Observation**

- If a blue coloration is produced, continue boiling of the first tube till complete hydrolysis of starch.
- After complete hydrolysis, cool and attempt tests of glucose.

**Reaction K**            **Water Solubility Test**

**Test-tube 10**

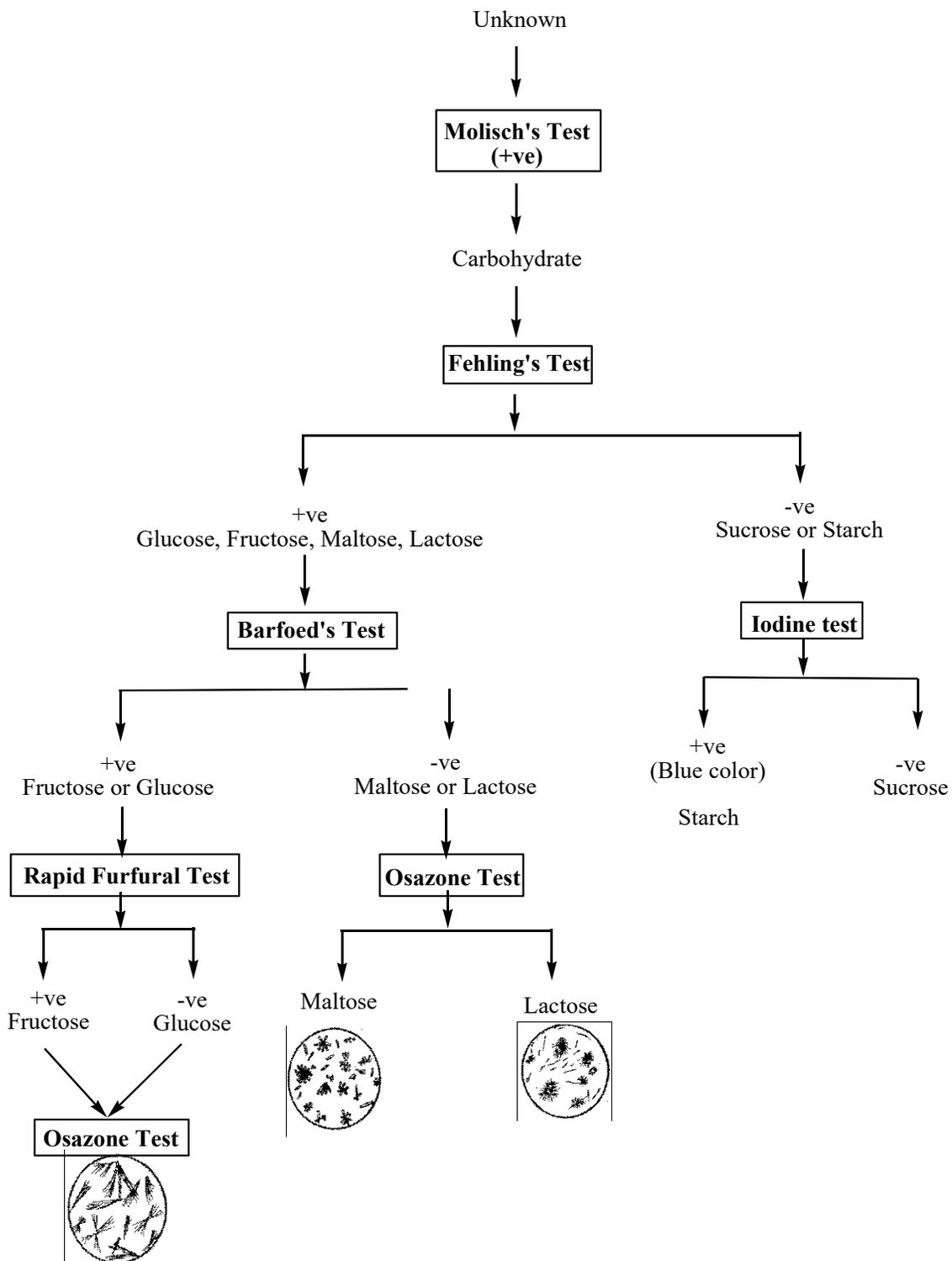
- Take solid sugar.
- Add water.
- Shake.

**Observation**

- Mono-and disaccharides are soluble in water.
- Starch insoluble in water.

## General Scheme for Identification of Carbohydrates

### Starch, Sucrose, Glucose, Fructose, Maltose, Lactose



**Report**

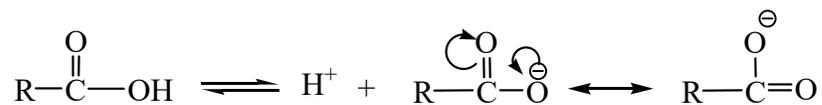
Physical Properties			
Color			
Shape			
Solubility			
Chemical Properties			
Test		Obs.	Res.
1			
2			
3			
4			
5			
6			
7			
8			
9			

**EXPERIMENT 9**

Date:

**Carboxylic acids and Their Derivatives****Reaction A      Reaction of Acetic Acid and Bicarbonate**

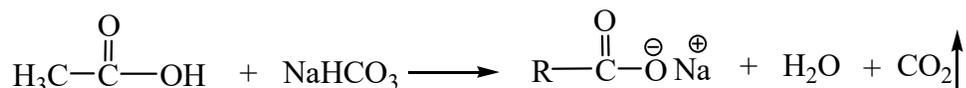
Carboxylic acids are stronger acids than phenols.

**Test-tube 1**

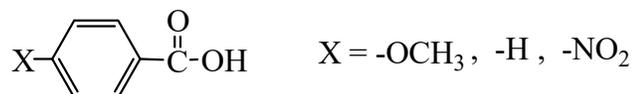
- Take 1 mL of 4% sodium bicarbonate solution.
- Add one drop of 90% acetic acid solution.

**Observation**

- .....
- Note the CO<sub>2</sub> evolved (effervescence).

**Reaction B      Relative Acidities of Some Substituted Benzoic Acid**

- o Electron withdrawing substituents in Ar will reduce the charge on the carboxylate anions.
- o The anion will therefore be stabilized.
- o The acid will therefore show a greater tendency to dissociate.
- o The acid will therefore be stronger if Ar is electron withdrawing than if Ar is electron donating.

**Take test-tubes 2, 3, 4**

- Place 1 mL of *p*-nitrobenzoic acid in test-tube 2.
- Place 1 mL of benzoic acid in test-tube 3.
- Place 1 mL of *p*-methoxybenzoic acid in test-tube 4.

- Add 1 drop of bromophenol blue solution to each tube.  
(pH color change of bromophenol blue; yellow (pH 3.0), blue (pH 4.6).
- Add 1 drop of 0.1M NaOH to each tube.

### Observation

- 1) Color of p-nitrobenzoic acid .....
- 2) Color of benzoic acid .....
- 3) Color of p-methoxybenzoic acid .....

### **Order of acidity:**

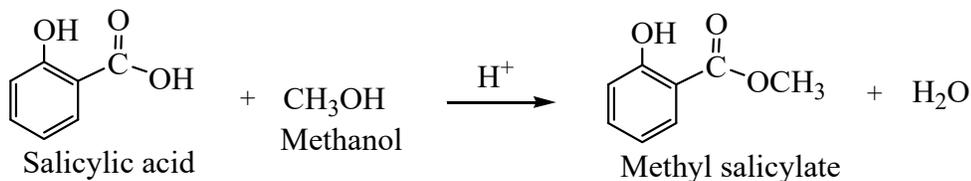
.....

### Reaction C      Esterification



### Take Test-tube 5

- Take 2 mL of the solution of sulfuric acid in methanol.
- Add 5 drops of the solution of salicylic acid in methanol.



- Place the tube in hot water bath.
- Take about 15 mL of cold water in a small beaker.
- Add the contents of the tube to the beaker.

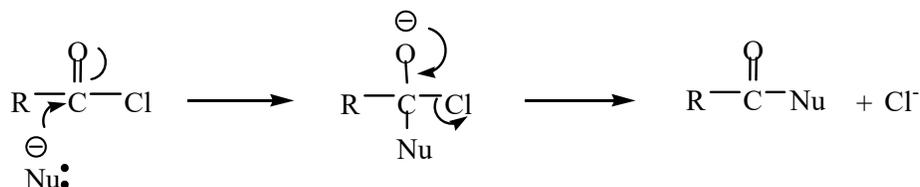
### Observation

.....

The ester, methyl salicylate (oil of wintergreen) has a distinctive smell.

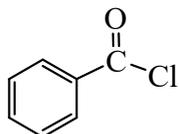
### Reaction D      Acyl Halide and an Amine

Acyl halides are the most reactive of the acid derivatives to nucleophile attack.

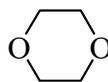


**Take Test-tube 6**

- Take 1 mL of benzoyl chloride solution in dioxan.



Benzoyl chloride

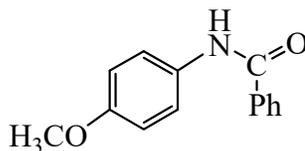
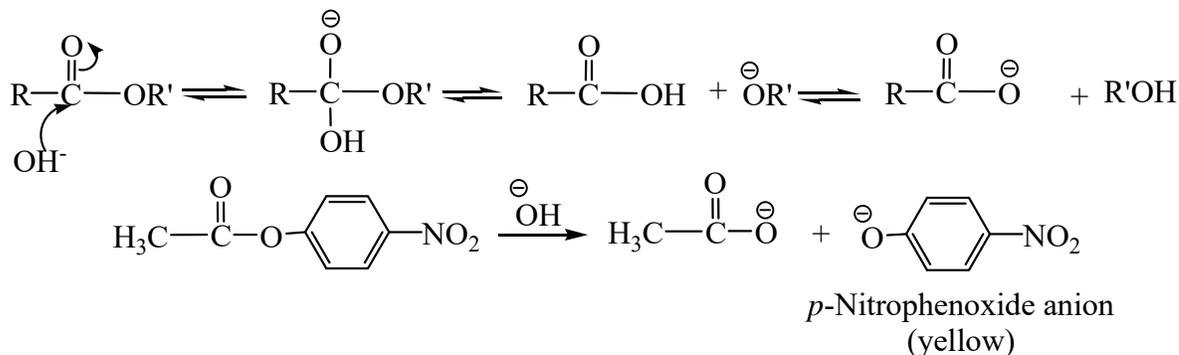


Dioxan

- Add 1 mL of the solution of *p*-methoxyaniline in aqueous ethanol.
- Allow to stand.

**Observation**

.....  
 .....

**Reaction E Ester Hydrolysis****Take Test-tube 7**

- Take 2 mL of tap water.
- Add 1 drop of 10% NaOH.
- Add 2 drops of the solution of *p*-nitrophenyl acetate in dioxin.
- Place the tube in the hot water bath.

**Observation**

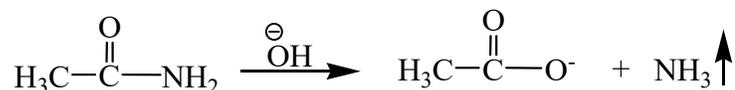
.....  
 .....

**Reaction F**      **Amide Hydrolysis**

Susceptible to basic (and acidic) hydrolysis but are less reactive than esters.

**Take Test-tube 8**

- Take 1 mL of the ethanol solution of acetamide.
- Add 1 mL of 10% NaOH solution.
- Place the tube in the hot water bath.



- Place a piece of moist red litmus paper at the mouth of the tube.

**Observation**

.....,  
.....,  
.....,

**Questions**

Write the chemical equation of the reaction for esterification reaction and hydrolysis of ester?

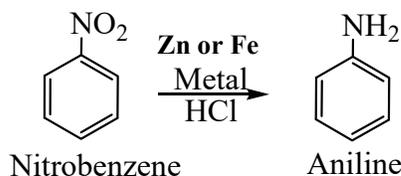
.....,  
.....,  
.....,  
.....,  
.....,  
.....,  
.....,  
.....,

**EXPERIMENT 10**

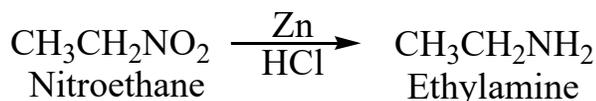
Date:

**Nitro and Amino Compounds****Reaction A      Reduction of the Nitro Group**

In the aromatic series this is the major synthetic route to primary amines,  
e.g.

**Test-tube 1**

- Take 2 mL of 1:1 conc. HCl: H<sub>2</sub>O (not conc. HCl).
- Add 5 drops nitroethane.
- Add the pieces of Zn provided.
- Place the tube in hot water bath.



- Add 10 mL of 10% NaOH to a 25 mL beaker.
- Pour the contents of the tube into this beaker.
- Swirl the beaker and place it on the hot plate.
- Describe the odor of the vapors.

Hold a dropper containing conc. HCl in the vapor over the beaker.

**Observation**

The product is .....

.....

**Reaction B      Basicity of Amines****Test-tube 2**

- Take 1 mL of aqueous aniline.
- Add 2 drops of phenolphthalein.  
(pH color change of phenolphthalein; colorless pH 8.0 to pink pH 10.0).



**Test-tube 4**

- Take 1 mL of the solution of aniline in 10% H<sub>2</sub>SO<sub>4</sub>.
- Slowly add 5 drops of NaNO<sub>2</sub> solution.
- Shake the tube after adding each drop.
- Set the tube aside.

**Reaction C (i)**      **Test-tube 5**

- Take 1 mL of 2-naphthol solution in sodium hydroxide.
- Pour a little (less than half) of the diazonium salt solution in Test-tube 4 into the 2-naphthol solution.

**Observation**

.....  
.....

**Reaction C (ii)**      **Test-tube 6**

- Take 10 mL of hot water.
- Add rest of the diazonium salt solution from Test-tube 4.
- Heat and swirl.

**Observation**

Detect the phenol by its odor

.....  
.....

**Reaction D**      **Bromination of Aniline**

Aniline is highly reactive to electrophilic substitution reactions (-NH<sub>2</sub> is a strong electron-donor).

**Test-tube 7**

- Take 3 drops of aqueous aniline solution.
- Add 1 mL of bromine water.

**Observation**

.....  
.....

**Questions**

1) Write the chemical equation for the bromination of aniline?

.....  
.....  
.....

2) Write the chemical equation for the hydrolysis of diazonium salt?

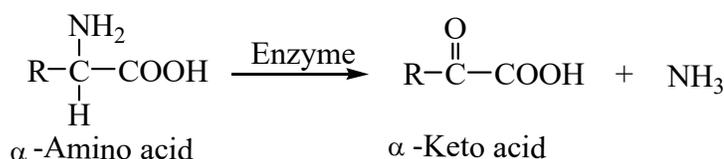
.....  
.....  
.....

## EXPERIMENT 11

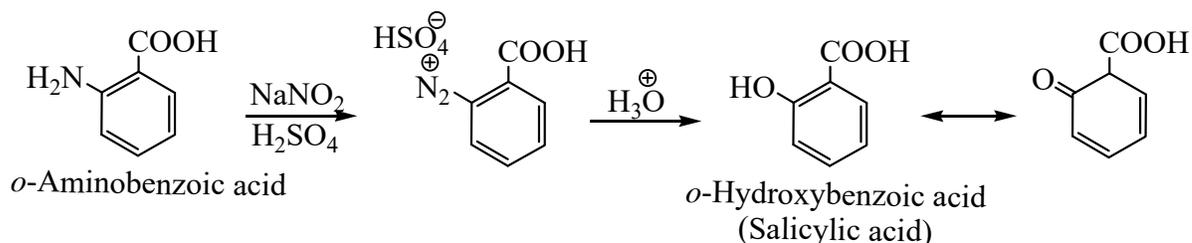
Date:

## De-Amination of Amino Acids

When an animal is starved for glucose, fats are used as energy source. If starvation is prolonged the body's stocks of fat begin to run down and finally they are exhausted. The only remaining substances present in the body which form oxidisable substances are protein. Such energy as the protein can provide comes through the oxidation of its constituent amino acids. The amino acid is deaminated (that is the amino-nitrogen is lost) and the resulting molecule is converted into substances on the direct pathway of either glucose or fatty acid oxidation.



In today's experiment we will deaminating an amino acid (*o*-aminobenzoic acid) using nitrous acid.



Diazotization (reaction with nitrous acid) of amino group will give a diazonium salt. The diazonium salt will react with water to give a phenol. So in this experiment we are deaminating  $\beta$ -amino acid to give the equivalent  $\beta$ -keto acid in its more stable enol form.

### Procedure

- In a 100 mL conical flask, warm a mixture of 2 g of *o*-aminobenzoic acid (anthranilic acid) and 20 mL of 10% sulfuric acid until the solid (the hydrogen sulfate salt of the basic amino group) just dissolves.
- Cool the reaction mixture in ice bath for a minute.
- Add 6 mL of 20% sodium nitrite solution to this mixture, with vigorous swirling. There is a vigorous, instant reaction.
- Without delay, pour this solution (now containing the diazonium salt) into a beaker containing 40 mL of 10% H<sub>2</sub>SO<sub>4</sub> in a 500 mL beaker.

- Stir the foamy product and heat on a hotplate until boils for 15 minutes, stir continually.
- Then add 50 mL of water and stir until a uniform color appears.
- Suction filter the product and recrystallize it from hot water.

Weight of *o*-hydroxybenzoic acid (salicylic acid) = ..... g.

m.p. of salicylic acid = .....°C.

### Questions

What is happen if you add sodium nitrate to aniline solution dissolved in sulfuric acid and why?

.....  
.....  
.....

Diazonium salts can be produced from the reaction of secondary and tertiary aromatic amines with nitrous acid, if NO, explain the expected products by chemical equation.

.....  
.....  
.....  
.....